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XIV. "Researches on the Phosphorus-Bases." No. X.—Metamorphoses of Bromide of Bromethylated Triethylphosphonium. By A. W. HOFMANN, LL.D., F.R.S. Received July 24, 1860.

Among the several products of transformation into which the bromide of bromethyl-triethylphosphonium is converted when submitted to the action of reagents, the substances formed by its union with bodies similar to ammonia, have hitherto almost exclusively occupied my attention. I have, however, of late examined a variety of other changes of this body, which deserve to be noticed.

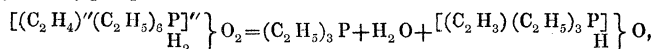
When heated, the bromide begins to evolve hydrobromic acid at a temperature of about 200°, which continues for a considerable length of time. The product of this reaction is evidently the bromide of vinyl-triethylphosphonium,



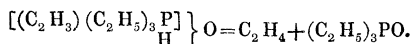
It is, however, difficult to obtain the substance pure by this process, since the temperature at which the last portion of hydrobromic acid is eliminated closely approximates the degree of heat at which the vinyl-body is entirely destroyed; and since the latter compound may be obtained with the greatest facility by other processes\*, I have not followed up any further this direction of the inquiry.

I have already mentioned, in a previous note, the deportment of

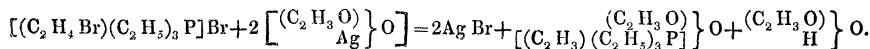
\* The hydrated di-oxide of ethylene-hexethyl-diphosphonium, when submitted to distillation, undergoes decomposition; two different phases are to be distinguished in this metamorphosis. At about 200° the base begins to disengage the vapour of triethylphosphine, the residuary solution retaining hydrated oxide of vinyl-triethylphosphonium,



the latter yielding at a higher temperature the oxide of triethylphosphine together with ethylene,

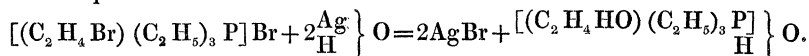


The vinyl-compound is even more readily obtained by the action of silver-salts, such as acetate of silver, at the temperature of 100°, on the bromethylated bromide.



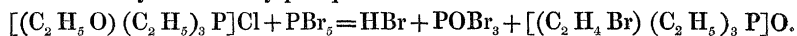
the bromethylated bromide with oxide of silver; the whole of the bromine is eliminated in the form of bromide of silver, a new base being formed.

According to circumstances, this base may be the vinyl-compound previously mentioned, or another body differing from the latter by containing the elements of one molecule of water in addition. This substance, which is always formed when the reaction takes place in moderately dilute solutions, is the oxide of a phosphonium, with three molecules of ethyl substituted for three equivalents of hydrogen, the fourth equivalent of hydrogen being replaced by an oxygenated radical  $C_2H_5O$ , arising from the radical  $C_2H_4Br$  by the insertion of  $HO$  in the place of  $Br$



I have fixed the nature of this compound by the analysis of the iodide, of the platinum-salt and of the gold-salt, and, moreover, by the study of several remarkable transformations which it undergoes when submitted to the action of reagents.

It appeared of some interest to ascertain whether the *oxethylated* might be reconverted into the *bromethylated* base. The chloride of the former is energetically attacked by pentabromide of phosphorus; oxybromide of phosphorus and hydrobromic acid are abundantly evolved, and the residue of the reaction contains the chloride of bromethylated triethylphosphonium.



Thus it is seen that the molecular group  $C_2H_5O$ , which we assume as hydrogen-replacing in this salt, suffers under the influence of pentabromide of phosphorus, alterations identical with those which it is known to undergo under similar circumstances, when conceived as a constituent of alcohol.

If we consider the facility with which the bromethylated triethylphosphonium is converted into the oxethylated compound, by the action of oxide of silver, and the simple re-formation of the first-mentioned body by means of pentabromide of phosphorus, a great variety of new experiments suggest themselves. As yet but little progress has been made in this direction; one of the reactions, however, which I have studied deserves even now to be mentioned.

The salts of bromethylated and oxethylated triethylphosphonium

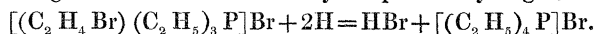
may be regarded as tetrethyl-phosphonium-salts, in which an equivalent of hydrogen in one of the ethyl-molecules is replaced by bromine and by the molecular group HO respectively.

Bromide of tetrethylphosphonium  $[(C_2H_4H)(C_2H_5)_3P]Br$ ,

Bromide of bromethylated tri-  
ethylphosphonium . . . . . }  $[(C_2H_4Br)(C_2H_5)_3P]Br$ ,

Bromide of oxethylated triethyl-  
phosphonium . . . . . }  $[(C_2H_4HO)(C_2H_5)_3P]Br$ ;

and the question arose, whether the bromethylated compound might not be converted, simply by reduction, into a salt of tetrethyl-phosphonium. This transformation may, indeed, be effected without difficulty. On acidulating the solution of the bromethylated bromide with sulphuric acid and digesting the mixture with granulated zinc, the latent bromine is eliminated as hydrobromic acid, its place being at the same time filled by 1 equiv. of hydrogen,



It was chiefly the facility with which a tetrethyl-phosphonium-compound may be obtained from the brominated bromide, that induced me to designate the hydrogen-replacing molecules  $C_2H_4Br$ , and  $C_2H_5O$ , which we meet with in the compounds above described, as *bromethyl* and *oxethyl*. It remained to be ascertained whether these compounds might actually be formed by means of direct substitution-products of ethyl-compounds. It was with the view of deciding this question that I have examined the deportment of triethylphosphine with the monochlorinated chloride and the monobrominated bromide of ethyl.

The former of these substances has been long known, having been investigated by Regnault many years ago; the latter had not been hitherto obtained. I have prepared it by submitting bromide of ethyl to the action of dry bromine under pressure\*. It is a heavy aromatic liquid boiling at  $110^\circ$ .

The chlorinated chloride and the brominated bromide of ethyl, although essentially different in their physical properties from dichloride and dibromide of ethylene, with which they are isomeric, nevertheless resemble the ethylene-compounds in their deportment with triethylphosphine.

In both cases the final product of the reaction is a salt of hexethyl-

\* In addition to the monobrominated bromide of ethyl,  $(C_4H_4Br)Br$ , there is also formed in this reaction the dibrominated bromide,  $(C_4H_3Br_2)Br$ .

ated ethylene-diphosphonium. I have identified these salts with those obtained by means of dichloride and dibromide of ethylene, both by a careful examination of their physical properties, and by the analysis of the characteristic iodide and of the platinum-salt. I have not been able to trace in the first of these reactions a salt of chlorethylated triethylphosphonium; but I have established by experiment that in the reaction between triethylphosphine and brominated bromide of ethyl, the formation of bromethyl-triethylphosphonium invariably precedes the production of the diphosphonium-compound.

XV. "Researches on the Phosphorus-Bases."—No. XI. Experiments in the Methyl- and in the Methylene-Series. By A. W. HOFMANN, LL.D., F.R.S. Received July 24, 1860.

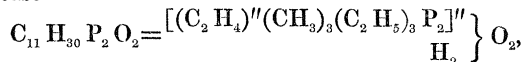
In former notes I have repeatedly called attention to the transformation of the bromide of bromethylated triethylphosphonium under the influence of bases. In continuing the study of these reactions, I was led to the discovery of a very large number of new compounds, the more important ones of which are briefly mentioned in this abstract.

#### HYBRIDS OF ETHYLENE-DIPHOSPHONIUM.

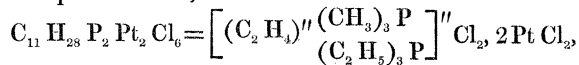
##### *Action of Trimethylphosphine upon Bromide of Bromethyl-triethylphosphonium.*

These two bodies act upon each other with the greatest energy, and moreover exactly in the manner indicated by theory. The resulting compound was of course examined only so far as was necessary to establish the character of the reaction.

The dibromide of the hybrid diphosphonium is more soluble than the hexethylated compound formerly described, which in other respects it resembles. Oxide of silver eliminates the extremely caustic base



which yields with hydrochloric acid and dichloride of platinum a pale-yellow platinum-salt,



separating in scales from boiling water.